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The Effect of Sodium Hexametaphosphate on Cottage Cheese Yields

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ON COTTAGE CHEESE YIELDS

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable for meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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INTRODUCTION

A major concern in the cottage cheese industry is the inefficient use of the available milk proteins. Currently, the methods of cottage cheese manufacture convert an average of only 74.9% of the milk proteins into cottage cheese, while the remainder are removed in the by-product whey (43, 56). As protein is the main determinant of both the yield and nutritional value of cottage cheese, if 25% of the available protein is lost to the whey, then potential cottage cheese yield and nutrition have been lost as well.

The proteins lost in the whey are mainly α-lactalbumin and β-lactoglobulin, which remain soluble during the conditions of cottage cheese manufacture and thus do not become part of the curd (38, 39). Although these proteins have the highest known nutritional value (21, 22, 45, 60, 71), they can be an added expense rather than a benefit to the dairy industry. The proteins as whey solids must either be processed further, disposed of, or both. Processing whey is expensive and difficult because cottage cheese whey is both dilute, 94% water, and highly acid, pH 4.6, (3, 9, 39, 65). Concurrently, the products produced by processing cottage cheese whey such as animal feeds, dried or concentrated products, and fermentation products have a limited and competitive market and are not highly profitable (39, 51). However, disposal is a less attractive and more expensive alternative because whey has a high biochemical oxygen demand (BOD) making it a major pollutant requiring high levels of microbial action for treatment (3, 10). Public response to whey as a pollutant has forced the passing of statutes forbidding the disposal of untreated whey into lakes, streams, and rivers. Concurrently, whey disposal in sewage systems has become increasingly expensive (3, 9, 39). The whey proteins, as part of the whey, thus present a temperamental enigma and overshadowing dilema to the cottage cheese industry: being the most nutritious proteins known, they remain virtually too unprofitable to process, but too expensive to throw away.

Recovery of some of the proteins dissolved in the whey is possible by the use of polyelectrolytes that will precipitate the whey proteins, allowing them to be recovered by centrifugation (25, 28, 33, 34). The substances reported to provide the largest recovery are carboxymethyl cellulose (CMC) and several phosphate compounds such as sodium hexametaphosphate (SHMP). If the procedures for recovering proteins from the whey using polyelectrolytes could be combined with the procedures for manufacturing cottage cheese, then the finished product would include the whey proteins, providing higher yields and nutritional value.

The objective of this study was to explore the possibility that polyelectrolytes may increase the yield of cottage cheese by removing proteins from the whey and adding them to the curd. The chosen additives were screened, and then the yields and composition of cottage cheese made by a widely accepted culture procedure (70) were compared with the yield and composition of cottage cheese made from milk containing 0.05 or 0.2% sodium hexametaphosphate.

LITERATURE REVIEW

Supplies and Uses of Cottage Cheese Whey

The potential gain in recovering the proteins present in cottage cheese whey is large, as the supply is assured by the steadily increasing consumer demand for cottage cheese (39, 44). Cottage cheese is a product of skimmilk coagulated by lactic acid to produce a soft, unripened curd that is subsequently cooked to reduce the moisture to 80% or less, washed, and creamed to not less than 4% milk fat for retail sale (29, 38, 51). Whey is the liquid remaining after the removal of the fat and protein from the milk during cheese manufacture (29, 38). Wheys include 85% of the volume of the milk used to make the cheese and contain 50 to 55% of that milk's nutrients (23, 38, 39). The average composition of cottage cheese whey is 93.5% water, 0.04% fat, 0.6% protein, 4.9% lactose, 0.8% ash (salts and minerals), and 0.4% lactic acid (11, 38, 39). Cottage cheese production assures a constant supply of whey, because for every kilogram (kg) of cottage cheese manufactured, 5.25 kg of whey are produced (44). During 1976, the production of 320 million kg (711 million lb) of cottage cheese resulted in 1,920 million kg (4,266 million lb) of whey containing 125 million kg (277 million lb) of solids (13). The whey solids included 75 million kg (165 million lb) of whey proteins, of which only 57% were used as human or animal food, or about 32 million kg (71 million lb) of whey proteins were left unused (3, 9, 13, 27, 39, 41, 44, 45, 60).

The whey proteins, α-lactalbumin and β-lactoglobulin, are excellent nutrients and are highly functional in food products (11, 21, 22, 23, 71). Using the protein efficiency ratio (PER) as a measure of nutritive quality, the whey proteins have the highest known rating, 3.2, compared to other well known proteins such as casein (the reference protein) 2.5, egg 2.6, corn 2.2, and soy 2.2 (71). The whey proteins contain all the essential amino acids in a readily digestible form and, although low in cystine, they are high in lysine, hence useful in supplementing vegetable proteins, especially cereal proteins (11). Further, the whey proteins are functionally useful when combined with other proteins by forming complexes that effectively bind water (11, 71).

Usage of the whey proteins however is hampered by problems incurred in recovery. Cottage cheese whey is dilute and contains relatively large amounts of calcium, phosphorus, and lactic acid (39). The lactic acid lowers the pH of cottage cheese whey to 4.4 to 4.6. While large quantities of lactic acid are needed to form a coagulum of the milk protein, casein, the high acid content of whey makes processing difficult and limits possible uses (11, 38, 39).

A common use of fresh or concentrated whey for hundreds of years has been as feed for livestock (11, 39). Schingoethe (59) has reviewed the literature on a use for whey as a replacement for drinking water for livestock. Generally, optimism was expressed as to the nutritional advantages and possible savings in feed costs. Farmers may also use whey as a fertilizer on their fields (39). However, due to the high salt content care must be taken with cottage cheese whey to prevent salt from building up in the soil.

Demand for the high acid whey from cottage cheese is very low, and it is usually rejected in its raw form by consumers and industry (39). Therefore, if a profitable use is to be found for acid whey the manufacturer must consider further processing (39). The first step is usually condensation or drying to lower transportation costs and improve the keeping quality (39). However, the high acid and lactose content of cottage cheese whey make conventional condensation and drying difficult. A successful drying method developed by United States Department of Agriculture researchers crystallizes about 75% of the lactose by concentrating the whey to 52% solids, cooling rapidly to 20 C, and holding it 18 h with constant agitation. The whey can then be spray dried with air injection (11).

Research on concentrating whey by ultrafiltration, reverse osmosis, electrodialysis, ion exchange, and gel filtration, in addition to conventional methods, has made impressive technical advancements (39). Ultrafiltration units capable of utilizing 200,000 kg of whey per day are presently operational (39). An advantage spurring the development of new manufacturing techniques is that the processes and operating temperatures (50-55 C) do not denature the whey proteins, therefore preserving the functional and nutritional characteristics of the proteins (39, 41).

The greatest demand for acid whey powders and concentrates is to supplement food products especially in the bakery and dairy industries. The bakery industry uses dry whey in breads and crackers, the lactose contributing to the desired golden brown crust while the proteins provide the proper texture. The dairy industry employs acid whey in sherbets using acid flavors (citrus fruits), fermented milks, cheeses, processed cheese foods, cheese dips and foods, and cheese powders (39). Other acid whey uses in the food industries include acid fruit beverages, salad dressings, and sausage binders (39).

Kosikowski (39) reported that acid whey is highly compatable with acid fruit juices, such as orange and pineapple. However, the use of large amounts of whey lead to a whey taint flavor and high salt cont nt. Hope was expressed that demineralized acid whey powder may overcome these problems.

An indirect use of whey is as a culture medium, fermented by microorganisms to produce specific end products such as alcohol, acetic acid, vitamins, antibiotics, and enzymes and/or to harvest the organisms themselves for use in human and/or animal foods (3, 9, 10, 38, 39, 41, 60).

Expanding research is increasing the uses for whey, however, the technology, equipment, labor, and handling needed to process whey requires such a large investment, that much of the whey produced is discarded (29, 38, 39). The solids that make whey nutritious also make that whey a major pollutant. Having a Biochemical Oxygen Demand (BOD) of 30,000 to 50,000 mg/ml (3, 10), one part of whey in 20 parts of water is sufficient to kill all fish in that environment, making the disposal of whey into lakes, streams, and rivers illegal (71). Further, the whey from a cheese plant handling 4500 kg (10,000 lb) of milk a day requires as much treatment as the effluent of a city of 16,900 inhabitants (65). The response of many sewage systems has been to either refuse to accept untreated whey or do so at increased rates (39, 71). Therefore, a manufacturer faces extensive restrictions and regulations and may have to go to great expense to dispose of his whey. Naturally, the manufacturer bears all the costs of transportation and handling of the whey, which is ultimately passed on to the consumer as higher prices.

Milk Proteins and the Cottage Cheesemaking Process

The manufacture of cottage cheese is based upon processes attempting to recover in the curd only one of milk's major protein components, casein. Therefore, the origins of inefficient protein recovery in the cottage cheese industry are inherent in the methods used to produce the cheese, which are tailored to the characteristics of the starting material, milk.

Milk is a complex mixture, containing the proteins, casein, α-lactalbumin, and β-lactoglobulin as colloidal suspensions, fat as an emulsion, and lactose and mineral salts in true solution with the continuous phase (11, 29). The average composition of milk used for cottage cheese making is 87% water, 3.3-3.5% protein, 3.5-4.0% fat, 5.0% lactose, and 0.7% ash, and mineral salts (11, 29). The cottage cheese making process deals exclusively with converting the casein from a colloidal suspension to curd, which is mainly casein and water (11, 29, 66). The fat is a valuable dairy product not desired in cottage cheese curd, so is removed from the milk prior to processing.

The whey proteins, lactose, and mineral salts are only accidently included with the curd in small amounts, the majority expected to be lost in the whey.

Casein is not a single protein, but a stabilized complex of subunit proteins tied together. The major casein fractions are α_{s1}, κ, β, and γ, which can be subdivided into further variants (11, 26, 29, 66). Casein exists in the milk as collections of approximately 10,000 subunits stabilized by calcium phosphate to form micelles 0.03 to 0.3 μm in diameter. The structure of the micelle is unknown, but several models have been theorized, some using κ-casein to stabilize the micelle (11, 19). The micelles exist as a colloidal suspension in milk, a large number of densely packed micelles, too large to go into solution yet small enough to be held in suspension by calcium ions (11, 19, 66). Substances in colloidal suspensions have varying degrees of affinity for water. Some, the hydrophobic colloids, have so little affinity for water that if the particle is not charged it will precipitate. Conversely, the hydrophilic colloid has sufficient affinity for water that even with no charge it will remain in suspension (4). The manufacture of cottage cheese is based upon the hydrophobic property of casein: that at the isoelectric point pH 4.6, the protein will have a net charge of zero and will not remain in suspension, but will precipitate (11, 47, 66). Thus by adjusting the pH of milk to the isoelectric point of casein the colloidal casein will precipitate from suspension and form a coagulum which can become cottage cheese (1, 11, 29, 38, 47, 70). The pH adjustment is accomplished by adding acid, either directly by direct acidification or indirectly through the use of selected strains of microorganisms that metabolize lactose to lactic acid (29, 47, 55). The coagulum that forms is cut into cubes that become the curd as the water and the dissolved materials are expelled as whey (11, 38). The expulsion of whey and firming of the fragile curd is accelerated by slowly increasing the temperature to 57 C (134 F) (38, 70).

Many variables occur during the manufacturing process which affect the quality of final cottage cheese (16, 18, 49, 54, 70). A manufacturer attempting to produce the highest quality cottage cheese curd should start with the highest quality skimmilk (38, 70). The milk should be high in casein and total solids because the yield is almost totally dependent upon the amount of casein present (1, 54). The milk should be as fresh as possible without flavor defects and free from antibiotics. Storage for several days even at low temperatures may allow sufficient psychrotrophic bacteria to develop undesirable fruity, bitter, putrid, and fermented flavors (1, 38, 70). The use of milk containing undesirable flavors will result in cottage cheese with undesirable flavors (1). Finally, the presence of antibiotics in cottage cheese milk will kill the starter culture organisms, ruining the cheese (70).

Currently, the milk is pasteurized at the lowest temperature and shortest time combination allowable to minimize the denaturation of β-lactoglobulin which complexes with κ-casein to produce a soft, fragile, and easily shattered curd (66). Attention is then given to carefully selecting and monitoring the starter culture to prevent gas production, bitter off-flavors, agglutination, and poor yields (1, 55). Because the culture organisms are susceptible to bacteriophage, they require care of preparation and proper rotation to prevent "dead vats" (55, 70). The coagulum should be cut as close to the isoelectric point of casein, pH 4.6, as possible (47). If the coagulum is cut at a higher pH, then the casein may not completely precipitate but forms a cohesive, tough, and rubbery curd. However, if the coagulum is cut at a lower pH, the casein may redissolve, forming a curd that shatters easily becoming soft and mealy (66). During processing, the proper cooking of the curd is essential to expel whey and develop the proper body and texture (1, 2, 66). If heat is applied too fast the proteins on the surface of the curd may denature, preventing whey in the curd from being released forming a mealy cheese (66). Finally, washing removes the acid whey taste from the cheese ; however, it is essential that the wash water be acidified to prevent shifting the pH of the curd enough to cause it to start redissolving (66). The wash water also may be chlorinated to 10 ppm to limit bacterial contamination.

The proteins, α-lactalbumin and β-lactoglobulin, account for 20% of the total milk protein, casein accounting for the other 80% (11, 29, 48). The average composition of the whey proteins is 55% β-lactoglobulin, 12% α-lactalbumin, 10% "proteose-peptone", 10 to 15% casein, and trace globulins and enzymes (48). The whey proteins remain in suspension at pH 4.6 the isoelectric point of casein, and will not become part of the cottage cheese curd (11, 38, 39). They can be denatured by heat, pH extremes, chemical precipitation, and mechanical shear (64). Heat denaturation produces the "cooked" flavor in milk, imparting increased heat stability following concentration, reduced stability to freezing, and resistance to clotting by rennin to the colloidal casein (48). When denatured, whey proteins may lose their solubility at the isoelectric point of casein or in salt solutions and will coprecipitate with casein (40, 48).

The application of heat to milk sufficient to denature the whey proteins causes an interaction to occur between K-casein and β-lactoglobulin. Excessive heat treatment applied to skimmilk used to make cottage cheese by conventional processes is undesirable, because the K-casein β-lactoglobulin interaction causes the loss of desired curd properties (48). However, with special care in setting, cooking, and handling curd coprecipitation can be used to increase yield while preserving desired curd characteristics (11, 48).

Precipitation of Whey Proteins with Polyelectrolytes

Whey as a source of protein has challenged researchers to find quick, simple, and efficient methods of recovering that protein without damaging the nutritional or functional properties. The use of heat, mechanical shear, and pH extremes will allow the recovery of the protein (48, 64), however desirable nutritional characteristics may be lost (41). A method that precipitates the whey proteins avoiding heat uses polyelectrolytes to bind with the proteins via electrostatic interaction and produce a flocculent precipitate at their isoelectric point (41). Mathur and Shahani (41) have reviewed the use of the polyelectrolytes, carboxymethyl cellulose, ferric chloride, ferripolyphosphate, polyacrylic acid, and sodium hexametaphosphate. Recoveries and composition are shown in Table 1. The proteins recovered by the cold precipitation process were reported to possess nearly all of their nutritional and functional characteristics, but to have an undesirably high ash content. However, a chemical treatment of sodium dithionite and gel filtration was reported to significantly reduce the ash contents of the protein concentrates.

One class of polyelectrolytes is the anionic gums such as locust bean gum, carrageenan, and carboxymethyl cellulose, often used as stabilizers in ice cream (24, 31, 61). Smith et al. (61) used anionic gums to recover the protein from soybean whey by forming insoluble complexes. Carrageenan at pH 4.5 was reported to recover 96% soybean protein. Goldman (24) noted that 0.25% anionic gum was capable of precipitating 2.5% whey protein at pH 4.6, but at other pH levels the whey proteins would only be precipitated by κ-carrageenan and carboxymethyl cellulose. Hansen et al. (28) and Hidalgo and Hansen (31, 32, 33) have reported on the use of carboxymethyl cellulose as a whey protein precipitant. They observed pH-dependent reactions between proteins and polyelectrolytes at an acid pH, usually below the isoelectric point of the protein. Maximum protein precipitation could be obtained when calculated amounts of protein and polyanion were matched, and the pH adjusted to form isoelectric aggregates. The interactions appeared

TABLE 1. Recovery and composition of whey protein concentrate (WPC) by cold precipitation technique.

Polyelectrolyte	Recovery of proteins	Composition of WPC	
		Protein	Ash
	----------	%	----------
Carboxymethyl cellulose	68.9	60.7	1.7
Ferric chloride	88.7	79.1	18.3
Ferripolyphosphate	91.7	69.5	28.4
Polyacrylic acid	63.3	82.0	12.9
Sodium hexametaphosphate	75.5	84.9	12.8

Source: Mathur, B. N., and K. M. Shahani. 1979. Use of total whey constituents for human food. J. Dairy Sci. 62:100. (41).

to be due to ionic attractions between oppositely charged colloids dependent upon pH and concentration. A typical recovery procedure involved the acidifying of acid whey to pH 3.2, diluting with an equal volume of 0.25% carboxymethyl cellulose (CMC) at pH 3.2, and centrifuging to recover the protein complex at 2 C. Recoveries (28) of 90% of the total protein were reported at pH 3.2 or the selective precipitation of β-lactoglobulin occurring at pH 4.0 and α-lactalbumin at pH 3.2. Excess polyanion caused the formation of soluble complexes, and high salt concentrations interfered with complex formation. The work by Cluskey et al. (14) supported the theory that hydrocolloids of the opposite charge would precipitate. A CMC concentration of 0.3-0.6% would precipitate 77% of the total milk protein at pH 6.8-6.9 with refrigeration temperatures. However, carboxymethyl cellulose stabilized the milk proteins at pH 4.6. Hill and Zadow (35, 75) further found that CMC was capable of precipitating 93% of the protein at pH 3.2.

The possibilities of using polyacrylic acid in recovering whey proteins were explored by Sternberg et al. (64). The advantages of using polyacrylic acid include recovery of the whey proteins virtually undenatured and the low cost of using a small concentration of inexpensive reagent. The recoveries for cottage cheese whey were 85.7% and 86.7% for sweet whey at pH 4.0 and 18 C.

Phosphate compounds offer promise as polyelectrolytes capable of recovering whey proteins (25, 30, 34, 37, 62). Spinelli and Koury (62) reviewed several phosphate compounds, the concentration, and pH needed to achieve maximum precipitation of fish proteins. Hexametaphosphate at 0.010 M was capable of precipitating about 70% of the fish proteins at pH 4.5. Gordon (25) was issued a patent for recovering protein with phosphate. The patent claimed that 0.2 g sodium hexametaphosphate was sufficient to recover all the protein in 100 ml whey. Hidalgo et al. (34) reported that 80% recoveries of whey proteins could be achieved at pH 3.0 and temperatures of 18 C with sufficient sodium hexametaphosphate.

Jones et al. (37) explored possibilities of protein recovery with ferripolyphosphate. Excellent recovery was reported using a pH range of 3.2 to 4.0.

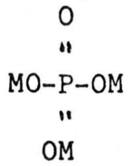
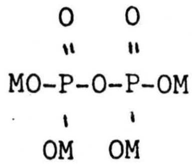
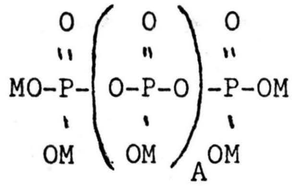
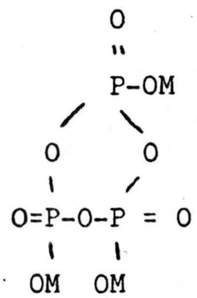
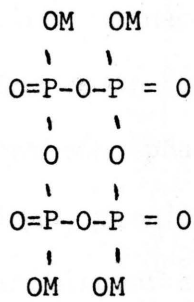
The addition of precipitants to milk to be made into cheese in the United States is limited to the salt, calcium chloride (72). Vorobyev (68) replaced calcium chloride with calcium phosphate $Ca(H_2PO_4)_2$ in milk to be made into Edam cheese. The addition of 0.03% calcium phosphate reportedly reduced the time need to coagulate the curd by rennet by 15 minutes, gave a more solid and elastic curd, accelerated curd processing, reduced the protein content of the whey, increased the yield by 5%, did not affect the pH of the cheese, did not affect the ratio of protein fractions soluble in water or a 5% solution of sodium chloride, and improved the quality of the ripened cheese. The addition of calcium phosphate was especially effective when added to low calcium milk.

The Chemistry of Phosphates

Phosphate compounds are natural constituents of nearly every food we eat (15). They have proved to be particularly useful in modifying foods and are routinely added to processed food products to affect such properties as texture consistency, uniformity, and appearance (15). Phosphates, as shown in Figure 1 are classified as orthophosphates, pyrophosphates, linear or straight chain phosphates, and cyclic phosphates (15, 67). All of the phosphates are surrounded by 4 oxygen atoms in a tetrahedral arrangement (67). The simplest phosphate compounds, orthophosphates, consist of such an arrangement of phosphorus and oxygen. Phosphoric acid and disodium phosphate are in this group (67). If from one to three of the oxygens surrounding a phosphate are shared with another phosphate, P-O-P, then the compound is known as a condensed phosphate. The simplest condensed phosphates contain 2 phosphorus and 7 oxygen atoms and are known as pyrophosphates. If the condensed phosphate contains 3 or more phosphorus groups, it will be either a linear or cyclic phosphate (53).

The linear or straight chain polyphosphates are condensed phosphates ranging in length from the 3 phosphate group trimer to long polymers. The cyclic phosphates termed metaphosphates, are composed of 3 to 4 phosphate groups (15, 67). All condensed phosphates when added to aqueous media undergo hydrolytic degradation, that eventually converts them to orthophosphates (67). The rate of conversion is regulated by the pH, temperature, presence of P-O-P hydrolyzing enzymes, catalysts such as multiply-charged metal ions, and the functionality of the pair of phosphate groups connected by the bridging oxygen undergoing attack (67). The hydrolysis rate is slow

FIG. 1. Structure of phosphoric acids. The letter M can be hydrogen or metal ion in the compounds used as food additives (15).

No. of Phosphates		Name
one		Orthophosphate
two		Pyrophosphate
$A = 1$ to 10^5		Linear Phosphates
three or four	 and	
		Cyclic Phosphates "metaphosphates"

in alkaline and neutral solutions, but increases with lower pH, higher temperatures, and enzymatic action (67).

Phosphates and polyphosphates (15) are added to food products to provide higher, lower, or buffered pH, ion sequesterization, nutritional supplementation, surface sorption, and polyelectrolyte behavior (15). The acid salts of ortho and pyrophosphates are good sources of acidity, and frequently used as acidulents in buffering systems. However, the long chain phosphates are not suitable for this purpose having a narrow buffering range while being difficult to prepare (67). The polyphosphates complex with metal cations in solution; sequestrants, preventing and inhibiting these ions from performing their normal functions (67). Additionally polyphosphates and orthophosphates can form insoluble salts with multiply charged metal ions, precipitating them out (67). Finally, polyphosphates have the ability of surface sorption or affecting the surface charge of a substance. If a substance has a large surface area, as in a colloidal dispersion, the polyphosphate may cause the deflocculation, dispersion, peptization, emulsification, or colloidal suspension of that substance (67).

Polyphosphates and proteins may react in complex manners, especially if the phosphate is a polyelectrolyte (67). A simplification of the process involves negatively charged polyphosphates complexing with the positively charged proteins at acid pH. If the pH of the solution is acid enough, negatively charged phosphate will combine with the positive charges on the protein, neutralizing the amino groups. Complexing the amine groups on the protein causes a shift in the association constants of the carboxylic groups that may affect the proteins structure and properties (67).

Sodium hexametaphosphate (SHMP) is a linear phosphate also known as glassy sodium metaphosphate, soluble sodium metaphosphate, and Graham's salt (15). Although now known to be a linear polyphosphate, it was erroneously believed to be a cyclic phosphate and given the wrong name and formula by the discoverer, Graham. Sodium hexametaphosphate is a common ingredient in foods and at low levels is recognized as safe when added to food products (15). Evidence has beer reported that SHMP may improve the digestibility of milk and milk foods for babies (15).

Effects of Phosphates on Milk Proteins

Large amounts of phosphates are used in the dairy industry, especially in processed cheeses in which up to 3% phosphate may be legally added (12, 15). The interactions of phosphates with milk proteins and the calcium ions that hold the micelles in suspension are extremely complex. While the addition of small amounts of a phosphate may stabilize milk proteins, preventing coagulation with the application of heat; the addition of larger amounts of the same phosphate may cause the milk proteins to precipitate (12, 15, 42).

The phosphates are used in cheese manufacture to sequester the calcium ions in starter mediums inhibiting bacteriophage, reduce coagulation time by rennet, give a more solid and elastic curd, accelerate processing, reduce the protein content of the whey, and increase yield (58). Processed cheeses use phosphates as emulsifiers;

8 out of the 13 emulsifiers allowed in processed cheeses are phosphates (15, 58). Phosphates are extensively used in instant pudding mixes to cause the added cold milk to gel and make the pudding possible. Typical mixes include trisodiumpyrophosphate with calcium acetate as a source of soluble calcium ions to cause the milk proteins to gel (15). Typically, the polyphosphates and orthophosphates retard gel formation when added to milk at low concentrations. However, when both are added at high concentrations gelling of milk proteins occurs, the rate being dependent upon the concentration of phosphate, calcium, and the casein complex, besides pH, temperature, amount of agitation, and type of phosphate counter ion present (15).

The long chained polyphosphates are well known protein precipitating agents, capable of precipitating both the casein and β-lactoglobulin protein fractions in milk (15). Sodium hexametaphosphate (SHMP) appears to have the greatest effect upon milk proteins; the κ-casein, the casein subunit thought to stabilize the casein micelle, being sensitive to attack by SHMP (42). Sodium hexametaphosphate also reacts with the calcium in milk reducing the milk's turbidity to lower levels than other calcium complexing agents. The addition of one part SHMP per 20 parts of casein in fluid milk is sufficient to cause the milk to lose opacity and become a yellow-green translucent serum. Sodium hexametaphosphate, being a large polyvalent anion, may bind with several proteins, forming larger particles or micelles (15). An acidic polyphosphate forming ionic bonds with the basic amino groups on the proteins will lower the proteins' net charge and cause those proteins to precipitate (15). The casein may combine in this reaction with a portion of the SHMP to form a stable large complex. If excess SHMP is added, then the excess may force the caseinate particles to release attached colloidal inorganic salts resulting in complete dispersion of the casein micelle, and loss of the opacity in the milk (15).

MATERIALS AND METHODS

Experimental Procedure

Three series of test vats were used to determine the feasibility of using polyelectrolytes to recover the whey proteins as cottage cheese curd. The experimental procedure consisted of manufacturing cottage cheese by the short set culture method (70), initially in 400 ml beakers and later in 3 liter stainless steel lab vats to screen potential additives and levels. Finally, cottage cheese was manufactured in 208 liter pilot plant vats simulating commercial production using the selected polyelectrolyte sodium hexametaphosphate at the levels of 0.05 and 0.2% by weight of skimmilk.

The primary screening employed 400 ml beakers as cottage cheese vats to evaluate the effects of sodium phosphate (Na_2HPO_4) at 0.05, 0.1, 0.2, and 0.5%; sodium hexametaphosphate at 0.05, 0.1, 0.2, and 0.5%; carboxymethyl cellulose at 0.025, 0.05, and 0.1%; and calcium chloride at 0.02 and 0.05% against a control skimmilk containing no additives. Nonfat dry milk, reconstituted to 10% solids at 32 C (90 F), was inoculated at 5% with fresh active lactic starter culture. The 300 g of the inoculated milk was weighed into a beaker and the appropriate amount of the component being tested was dissolved in the milk using a blender. The beaker vats were subsequently processed by the short set culture method for manufacturing cottage cheese (70) up to and including draining; the curd was cut at pH 4.7 with a spatula and cooked at 50-56 C (122-133 F). Samples were taken of the milk curd and whey for evaluation (FIG. 2.).

FIG. 2. Flow diagram of the screening test exploring the effects of precipitating aids on cottage cheese.

Reconstituted NFDM

10% Solids

Beaker Vats
400 ml

Control | Experimental

Laboratory Vats
3 liters

Control | Experimental

Additive

0.05, 0.1, 0.2, 0.5%, Sodium phosphate (Na_2HPO_4), 0.05, 0.1, 0.2, 0.5%
0.05, 0.1, 0.2, 0.5%, Sodium hexametaphosphate (SHMP), 0.05, 0.1, 0.2, 0.5%
0.025, 0.05, 0.1%, Carboxymethyl cellulose (CMC), 0.05, 0.1%
0.02, 0.05%, Calcium chloride ($CaCl_2$)

Short Set Cottage Cheese

Cut pH 4.7

Cook

Wash

Weigh and Sample

The secondary screening used 3 liter laboratory vats to evaluate the yield performances of skimmilk containing sodium phosphate (Na_2HPO_4) at 0.05, 0.1, 0.2, and 0.5%; sodium hexametaphosphate at 0.05, 0.1, 0.2, and 0.5%; and carboxymethyl cellulose at 0.05 and 0.1% compared to a control skimmilk containing no additives. Three vats could be made at one time, two containing different levels of an experimental additive and one being the control. Each vat was filled with 2.5 kg of 10% solids reconstituted nonfat dry milk at 32 C (90 F), and inoculated with fresh active lactic acid producing starter culture at 5% level (125 g). The milk was then processed into cottage cheese by the short set culture procedure (70), with the curd being cut at pH 4.7 and cooked to 50-56 C (122-133 F). Samples of milk, curd, and whey were collected in 236.4 ml (8 oz) Whirl-Pak plastic bags for further analysis, (Fig. 2).

Sodium hexametaphosphate at the levels 0.05 and 0.2% by weight of skimmilk was chosen for further study following the evaluation of the screening tests. The cottage cheese was made in 208 liter (55 gal) pilot plant vats, using the short set culture method (70) as shown in Fig. 3.

Fresh skimmilk from the South Dakota State University Dairy Products Laboratory was transferred to a pasteurizing vat and heated to 43.3 C (110 F). Nonfat dry milk was added via a powder funnel to fortify the skimmilk by 0.5% solids by weight of the skimmilk. The skimmilk was subsequently vat pasteurized by a heat treatment of 63 C (145 F) for 30 minutes followed with immediate cooling to 3-4 C

FIG. 3. Flow diagram of cottage cheese manufacturing process in 208 liter pilot plant vats.

Fresh Skim Milk

Fortification with 0.5% NFDM

Pasteurization with 60 C for 30 min.

Bulk Starter 5%

Control

Sodium hexametaphosphate

0.05%
0.2%

Short Set Cottage Cheese

Cut pH 4.7

Cooked 50-56 C

Drained

Weighed

(37-39 F) by a plate cooler. Finally, the skimmilk was transferred into sanitized 37.8 liter (10 gal) milk cans and stored overnight at 2-3 C (35-37 F).

The mother culture was prepared from commerically available lyophilized strains of lactic acid producing streptococci bacteria. The medium were prepared by adding 100 ml of 10.5% total solids reconstituted nonfat dry milk to dilution bottles. The culture medium received subsequent heat treatment of 86 C (187 F) for 45 minutes in a steam cabinet, followed with cooling to either 21 C (70 F) for immediate inoculation or 4-5 C (39-41 F) for storage. The culture was started by inoculating the lyophilized bacteria strains into a prepared medium blank at 21 C (70 F) and incubating it for 12-14 hours at 21 C (70 F) to achieve the desired acidity development of 0.70-0.85%. Upon completion of incubation, 1% transfers were made into 4 C (39 F) media blanks, which would be held at 4 C until their incubation at 21 C for 12-14 hours. Subsequent transfers were made daily to build and maintain the activity of the starter culture (7, 8, 57, 71).

Culture for the cheese was prepared using 1% transfers from the mother culture to 17.1 kg (38 lb) of the previously prepared skimmilk. Prior to inoculation this skimmilk received an additional heat treatment of 86 C (187 F) for 45 minutes in a steam cabinet, followed by immediate cooling to 21 C (70 F). Following inoculation from the mother culture, the starter was incubated at 21 C for 12-14 hours to achieve the desired pH of 4.40-4.55 (titratable acidity 0.70-0.85%).

The manufacture of the cottage cheese was initiated by splitting the processed skimmilk equally between two sanitized 208 liter (55 gal) vats, with 141.75 kg (315 lb) in each. The temperature of the milk in both vats was raised to 32.2 C (90 F). Starter culture was then added to the west vat, at the rate of 5.2% by weight, and thoroughly mixed with the skimmilk. The same procedure was then repeated 15 minutes later by adding culture to the east vat, making the processing of the vats 15 minutes apart. Fifteen minutes after the addition of the culture, 1 to 2 liters (1.06-2.12 qt) of milk were removed from the vat that was to receive the added sodium hexametaphosphate[1] and transferred to a sanitized stainless steel beaker containing the proper amount of previously weighed sodium hexametaphosphate. The sodium hexametaphosphate was stirred into the milk until it was completely dissolved. This solution was then added to the vat and thoroughly mixed into the milk. Coagulator, consisting of 1 ml Angevines cottage cheese coagulator[2] diluted to 20 ml with water was added to each vat 30 minutes after it had received starter. The vats were then covered and allowed to remain undisturbed. Samples were taken periodically for pH and titratable acidity (TA) measurements, 10 to 15 cm (4-6 in) below the surface of the coagulum with sterile pipettes. When the pH of the coagulum dropped to 4.7

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[1] Polyphos[R]. Sodium hexametaphosphate. Olin Chemicals, 120 Long Ridge Road. Stanford, CT 06904.

[2] Angevine - Funke, Inc., 3380 Tree Court Industrial Boulevard. St. Louis, MO 63122.

(TA .49-.51) the curd was cut with sanitized 0.64 cm (1/4 in) knives, beginning with lengthwise cuts with the horizontal knife. Lengthwise cuts with the vertical knife, followed by cross cuts using the vertical knife completed the cutting. The curd was then allowed to sit undisturbed for 15-20 minutes to heal. The curd was then cooked, the temperature of the vat being raised a specific level during 15 minute periods: 2.8 C (5 F) in the 1st 15 minutes, 6.7 C (8 F) for the 2nd 15 minutes, 5.6 C (10 F) during the 3rd 15 minutes, and 6.7 C (12 F) per 15 minutes until completion of cooking. The cooking end point was determined by observing the firmness of the curds after several had been cooled to 10 C (50 F). Upon completion of cooking the curds were held in the hot whey approximately 20 minutes. Before draining the curd was allowed to sit unstirred for the last 5 minutes to allow the fines to settle. Then the whey was drained to the level of the curd and 76 liters (20 gal) of wash water added to the vat (17). The wash water was previously prepared by acidifying water to pH 5 with phosphoric acid, adding chlorine to the level of 10 ppm, and plate cooling the water to 3-4 C (37-39 F). The curd was allowed to remain 15-20 minutes in the wash water, then the vat was drained to the level of the curd and a second wash of 114 liters (30 gal) wash water added. After 15-20 minutes the curd was drained and ditched for at least 30 minutes, and then mixed, sampled, and transferred to 11.4 liter (3 gal) containers and weighed for yield determination. The curd was then creamed and frozen.

Sample Collection

The milk used in the cottage cheesemaking was sampled in duplicate. Whey and the wash waters were collected in a tared 37.8 liter (10 gal) milk can, weighed, and thoroughly mixed. One sample of each whey and wash water was collected for determination of curd fines, and two additional whey samples were taken for compositional analysis. The curd was thoroughly mixed after draining and duplicate representative samples taken. All samples were stored in 532 ml (18 oz) Whirl-Pak plastic bags.

Composition Analysis

Identical procedures were followed for the determination of the total solids, fat, solids-not-fat (SNF), lactose, ash, phosphorus and calcium contents of the milk, curd, and whey samples. Determination of total solids was by the Mojonnier method as described by Atherton and Newlander (6). Fat analysis was by the AOAC Roese-Gottlieb method (5), with solids-not-fat calculated as the difference between the total solids and fat. Protein content of the curd was determined by Mickelsen's procedure (43) of blending 25 g of curd with 75 g of 0.05 M sodium hydroxide prior to analysis. The AOAC Kjeldahl procedure (5) was then used to determine the protein content of the milk, whey, and curd, with Roland's procedure (52) being used for determination of casein and whey proteins. The ash content was determined by the AOAC official method (5). Lactose was determined as the difference between the solids-not-fat and the sum of the total of protein and ash. The samples for mineral analyses were prepared by dry ashing, then dissolved in 2 ml concentrated hydrochloric acid and diluted to 100 ml with distilled water. Phosphorus was determined by a colorimetric procedure (46). Calcium was determined by atomic absorption spectrophotometry using the sample prepared in the same manner as for the phosphorus determination.

Quantification of the amount of curd lost as fines was determined by Satterness's modification (66, 67) of Robb's procedure (50).

Expression of Yield

Yields were expressed as kg 20% solids curd per 100 kg milk, kg 20% solids curd per kg milk solids, and percent recovery of milk solids in the curd.

Statistical Analysis

Statistical analysis of the data utilized the least squares analysis of variance for a two factor (added SHMP and replication) design experiment (63).

RESULTS AND DISCUSSION

Cheese Milk Composition

The potential yield of cottage cheese is directly related to the composition of the starting milk, particularly to the quantity of casein present (1). The composition of the milk used in this study is given in Table 2. During the testing each level of added sodium hexametaphosphate (SHMP) was compared solely to a control containing no SHMP. Thus cottage cheese containing 0.05% added SHMP was compared to a control cottage cheese manufactured from the same milk, culture, and environmental conditions. The 0.2% SHMP level was likewise compared in cottage cheese to a separate control. However, the 0.05 and 0.2% SHMP cottage cheeses were not compared to each other, nor to the same control; instead each pair of variables was considered separately.

The total solids content of the milks used in this study was higher than expected for skimmilk. Although, normally the total solids content of skimmilk is 9.5% (29, 57), the milk used for the 0.05% SHMP and control cottage cheese had a total solids content of 10.33%. The total solids for the 0.2% SHMP and control skimmilk was also high at 10.26%. The high total solids was due to the high fat content of the milk used, 1.17 and 1.26% fat respectively for the 0.05 and 0.2% SHMP milks versus the target fat content of 0.1%. Inefficiency of the separator in removing the fat from the relatively small amounts of milk used in this study was responsible for this high fat content.

Fortification of the milks with nonfat dry milk increased the

TABLE 2. Composition of the milk used in the manufacture of cottage cheese.

Component	0.05% SHMP and Control[a]	0.2% SHMP and Control[a]
	%	
Total solids	10.33	10.26
Fat	1.17	1.26
SNF	9.16	8.99
Total protein	2.81	2.91
Casein protein	2.28	2.36
Whey protein	0.54	0.54
Lactose	5.62	5.36
Ash	0.73	0.73
	mg/100ml	
Phosphorus	88.98	92.08
Calcium	106.46	114.50

[a]Means of 8 replications.

solids-not-fat (SNF) levels to 9.16% for the 0.05% SHMP milk and 8.99% for the 0.2% SHMP milk which was close to the target value of 9.00%. However, the protein content of both milks was lower than the expected values of 3.5% total protein, 2.8% casein, and 0.7% whey protein (29). The 0.05% SHMP milk contained 2.81% total protein, 2.28% casein, and 0.54% whey protein, and the 0.2% SHMP milk contained 2.91% total protein, 2.36% casein protein, and 0.54% whey proteins. The lactose was higher for both experimental milks than has been reported: 5.62% for the 0.05% SHMP milk and 5.36% for the 0.2% SHMP milk versus the reported average of 4.9% (29).

The low protein content may have been due to obtaining the milk used during the summer months, when the protein content is usually the lowest (36). Another factor is that dairy animals are being selected and bred to produce offspring genetically capable of yielding larger quantities of milk. However, the milk obtained from animals breed for higher production contains smaller percentages of protein, a problem currently facing milk processors (74). The increase in lactose may have been caused by fortifying the milk with nonfat dry milk, which is concentrated skimmilk added to increase the protein in the milk and contains 52.3% lactose (29).

The ash content of all the milks used was 0.73%, close to the expected value of 0.7% (29). The observed quantities of phosphorus and calcium in the experimental milks were within the range of commonly reported values. The phosphorus content of the 0.05% SHMP milk was 88.98 mg/100 ml and the 0.2% SHMP milk contained

92.08 mg/100 ml versus reported values ranging from 90 to 112 mg/100 ml (29, 69). The calcium content for the 0.05% SHMP was 102.46 mg/100 ml and 114.50 mg/100 ml for the 0.2% SHMP milk. Though reported values average around 120 to 121 mg/100 ml, Feeley et al. (20) have noted a wide variation of mineral quantities reported in milk. They found that milk was reported to contain levels of calcium ranging from 101 to 137 mg/100 ml.

Curd Composition

The composition of the cottage cheese curds produced in this study is shown in Table 3. The mean squares used in calculating the probability that significant differences occurred amongst the curd components are presented in Tables 4 and 5. The composition of the cottage cheese curds produced in this study as a group differed from the average cottage cheese curd composition. The total solids content of cottage cheese curd is usually 21% (29). However, the mean total solids of the curds produced in this study, 26.14, 25.36, 24.59, and 24.88%, were unusually high. The major factor contributing to this increase was that the high fat values of the starting milk resulted in unusually high fat values in the cottage cheese curd. The 0.05% SHMP and control curds contained 5.15 and 4.80% fat respectively; higher than the average cottage cheese curd fat content of 0.4% (29). Although the total solids increased, the high curd fat content caused the protein fractions, normally totaling 16.9% (29), to decrease. Because this high fat cottage cheese curd is different from skimmilk cottage cheese curd there may be doubt concerning the results of this study. However, since both the control and SHMP treated curds were made from the same milk, the effect of the SHMP treatment should be visible and the results valid.

Significant differences ($P<.01$) occurring between cottage cheese curds made from milk with and without SHMP at 0.05% were revealed in the ash, phosphorus, and calcium fractions. The treatment of milk with 0.05% SHMP with subsequent manufacture into cottage cheese produced a curd containing higher ash (0.31%), phosphorus (71.11 mg/100 mg), and calcium (66.55 mg/100 mg) levels.

Significant differences ($P<.01$) occurring between the 0.2% SHMP and its control cottage cheese were in the fat, solids-non-fat, total protein, casein, lactose, ash, phosphorus, and calcium. The addition of 0.2% SHMP to milk subsequently made into cottage cheese produced a curd higher in solids-non-fat (0.94%), lactose (2.29%), ash (0.72%), phosphorus (230.15 mg/100 mg), and calcium (174.10 mg/100 mg); and lower in fat (0.94%), total protein (2.06%), and casein (2.09%). Because the whey protein content did not decrease, the decrease in total protein appears due to the decrease in casein.

The effect of SHMP upon cottage cheese was to produce a curd containing larger quantities of ash, phosphorus, calcium, and with increasing levels of SHMP more lactose. The greater the amount of SHMP added, the greater the increase of these curd components in the cottage cheese. However, with increasing addition of SHMP the possibility increases that the curd may have lower percentages of

TABLE 3. Composition of curd resulting from the manufacture of cottage cheese made with and without sodium hexametaphosphate (SHMP).[a]

Component	Control[b]	0.05% SHMP[b]	Control[b]	0.2% SHMP[b]
		---%	---	
Total solids	26.14	25.36	24.59	24.88
Fat	4.80	5.15	5.27	4.33**
SNF	15.20	14.85	14.73	15.67**
Total protein	11.99	11.02	12.82	10.76**
Casein protein	11.72	10.69	12.48	10.39**
Whey protein	0.28	0.33	0.34	0.36
Lactose	2.73	3.04	1.39	3.68**
Ash	0.48	0.79**	0.52	1.24**
		---mg/100g---		
Phosphorus	163.94	235.05**	150.86	381.01**
Calcium	70.16	136.71**	66.81	240.91**

[a]All curd components except total solids are calculated to a 20% total curd solids basis.

[b]Means of 8 replications.

**Highly significant (P<.01).

TABLE 4. Mean squares determining statistical significance between 0.05% SHMP and control cottage cheese curd components.

Source of variation	Degree of freedom	Curd Component Mean Squares									
		Total solids	Fat	SNF	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
Treatment	1	4.9141	0.4935	0.4935	3.7636	4.2025	0.0121	0.3938	0.3721	20235.0625	17695.6506
Replication	7	20.9203	0.8433	0.8433	1.0063	1.0085	0.0112	0.3249	0.0060	2049.0295	642.6613
Treatment x Replication	7	1.8584	0.1007	0.1007	0.7882	0.7671	0.0033	0.7685	0.0040	560.8154	215.7878
Residual	(16, 0)[a]	0.0126	------	------	------	------	------	------	------	----------	----------

[a]Residual degree of freedom is 16 for curd total solids, 0 for other curd components.

TABLE 5. Mean squares determining statistical significance between 0.2% SHMP and control cottage cheese curd components.

		Curd Component Mean Squares									
Source of variation	Degree of freedom	Total solids	Fat	SNF	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
Treatment	1	0.6328	3.5910	3.5910	17.0776	17.4515	0.0020	21.0911	2.0592	211853.0756	121243.24
Replication	7	15.5215	0.3351	0.3351	0.9575	1.1552	0.0140	0.8528	0.0193	2262.0341	1149.8796
Treatment x Replication	7	0.0710	0.0043	0.0549	0.0011	0.0009	0.0023	0.0477	0.0016	449.4756	637.42
Residual	(16, 0)[a]	0.0116	-------	------	-------	-------	------	-------	------	-----------	----------

[a]Residual degree of freedom is 16 for curd total solids, 0 for other curd components.

casein and fat. The increase in ash was in agreement with the findings of Mathur and Shahani (41) who noted an increase in the ash content of whey protein concentrates prepared by precipitation with polyelectrolytes including SHMP. The increase in curd phosphorus and calcium has been reported by Wong et al. (73). They noted that adding SHMP to milk manufactured into cottage cheese increased the phosphorus and calcium levels producing a nutritiously more desirable calcium to phosphorus ratio (1:1.5) compared to that of regular cottage cheese (1:3.4). Although the whey protein fractions were higher in the SHMP curds (0.02 and 0.05%) these differences were not statistically significant ($P<.05$).

Whey Composition

The composition of the wheys produced in this study is given in Table 6. The mean squares used to calculate statistical significance between whey components are presented in Tables 7 and 8. The wheys produced in this study contained higher percentages of total solids, fat, and lactose, and lower quantities of total proteins than previously reported (39, 57). The average composition of cottage cheese (acid) whey is 6.5% total solids, 0.4% fat, 0.75% total protein, 4.9% lactose, 0.4% lactic acid, and 0.80% ash (39). However, the wheys produced in this study had compositional ranges of 6.68 to 6.98% total solids, 0.22 to 0.36% fat, 0.48 to 0.55% total protein, 5.24 to 5.41% lactose, and 0.66 to 0.73% ash.

Whey originating from cottage cheese made with and without 0.05% SHMP showed no significant differences ($P>.05$) between any of the

TABLE 6. Composition of whey resulting from the manufacture of cottage cheese with and without sodium hexametaphosphate (SHMP).

Component	Control[a]	0.05% SHMP[a]	Control[a]	0.2% SHMP[a]
		%		
Total solids	6.78	6.72	6.68	6.98*
Fat	0.24	0.22	0.23	0.36**
SNF	6.54	6.50	6.44	6.62
Total protein	0.55	0.51	0.51	0.48
Casein protein	0.08	0.06	0.08	0.09
Whey protein	0.46	0.45	0.43	0.40
Lactose	5.34	5.30	5.24	5.41
Ash	0.66	0.69	0.70	0.73
		mg/100ml		
Phosphorus	73.93	75.99	73.53	87.24
Calcium	109.37	100.41	104.20	80.75

[a]Means of 8 replications.

*Significant ($P<.05$).

**Highly significant ($P<.01$).

TABLE 7. Mean squares determining statistical significance between 0.05% SHMP and control cottage cheese whey components.

		Whey Component Mean Squares									
Source of variation	Degree of freedom	Total solids	Fat	SNF	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
Treatment	1	0.0344	0.0014	0.0095	0.0060	0.0025	0.0008	0.0053	0.0028	16.81	322.2025
Replication	7	1.4416	0.0134	0.6802	0.0043	0.0030	0.0021	0.5302	0.0082	16.0868	53.6282
Treatment x Replication	7	0.8256	0.0039	0.4650	0.0034	0.0030	0.0025	0.3847	0.0059	41.2914	69.8282
Residual	(16, 0)[a]	0.0006	------	------	-------	------	------	-------	------	-------	--------

[a]Residual degree of freedom is 16 for whey total solids, 0 for other whey components.

TABLE 8. Mean squares determining statistical significance between 0.2% SHMP and control cottage cheese whey components.

		Whey Component Mean Squares									
Source of variation	Degree of freedom	Total solids	Fat	SNF	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
Treatment	1	0.7503	0.0689	0.1208	0.0025	0.0002	0.0018	0.1139	0.0036	23.7656	479.61
Replication	7	0.8397	0.0122	0.4164	0.0038	0.0021	0.0051	0.2670	0.0095	550.3778	730.8896
Treatment x Replication	7	0.0710	0.0043	0.0549	0.0011	0.0009	0.0023	0.0477	0.0016	449.4756	637.42
Residual	(16, 0)[a]	0.0009	------	------	-------	------	-------	------	------	--------	--------

[a]Residual degree of freedom is 16 for whey total solids, 0 for other whey components.

components tested. However, whey originating from cottage cheese made with 0.2% SHMP contained significantly higher levels of total solids, 0.3%, (P<.05) and fat, 0.13%, (P<.01) than its control. The lower quantities of fat in 0.2% SHMP curd, and the correspondingly larger amounts of fat in its whey indicate that the addition of large amounts of SHMP into cottage cheese manufacture may cause some fat loss from the cheese curds. However, because cottage cheese is normally made from skimmilk, fat loss would not be a problem. The SHMP whey contained smaller quantities of whey protein (0.03%), but the difference was not significant (P<.05).

Yield Lost as Curd Fines

The amount of curd lost in the whey as curd fines is given in Table 9, with the mean squares used to determine significant differences presented in Table 10. The observed curd fine losses for all wheys are lower than the fine losses of 1.55 kg 20% solids curd per 100 kg milk reported by Satterness et al. (57) for fortified skimmilk manufactured into cottage cheese by the short set culture method. No significant differences in the amounts of yield lost as curd fines in the whey and both wash waters compared both individually and totaled, occurred between cottage cheese treated with 0.05% SHMP and its control. No significant differences in the amount of yield lost as curd fines were present in the whey and wash waters of 0.2% SHMP and its control cottage cheese. The addition of SHMP to milk subsequently made into cottage cheese curd did not cause or protect from increased shattering of the curd, which would be measured as an

TABLE 9. Average yield lost as curd fines in cottage cheese whey and wash waters.

Source of yield loss	Yield lost (kg 20% solid curd/100 kg milk)			
	Control[a]	0.05% SHMP[a]	Control[a]	0.2% SHMP[a]
Whey	0.67	0.73	0.61	0.55
First wash	0.25	0.24	0.20	0.24
Second wash	0.18	0.23	0.20	0.18
Total	1.10	1.20	1.01	0.96

[a]Means of 8 replications.

TABLE 10. Mean squares determining statistical significance between SHMP treated cottage cheese and their controls for yield lost as curd fines.

		0.05% SHMP and Control Mean Squares			0.2% SHMP and Control		
Source of variation	Degree of freedom	Whey	Wash Water 1	Wash Water 2	Whey	Wash Water 1	Wash Water 2
Treatment	1	0.0020	0.0001	0.0090	0.0150	0.0052	0.0012
Replication	7	0.2984	0.0270	0.0107	0.2278	0.0070	0.0041
Treatment x Replication	7	0.0371	0.0463	0.0100	0.0519	0.0080	0.0019

increase in yield lost as curd fines.

Cottage Cheese Yield

The yields for the cheese produced in this study are presented in Table 11. The mean squares used to determine the statistical significance between comparisons are presented in Table 12. Cottage cheese yields are commonly expressed as kg of 20% solids curd per 100 kg milk. However, this expression does not show how efficiently the manufacturing procedure was at converting the solids available in the milk to cottage cheese. Therefore yield is also expressed as kg 20% solids curd per kg of milk solids and as percent recovery of milk solids. Together, the three methods of yield determination used serve to complement each other, and provide a complete picture of the yield (1).

Cottage cheese made from milk containing 0.05% SHMP showed significantly higher yields ($P<.05$) when yield was expressed as kg 20% solids curd per 100 kg of milk (0.77 increase) and as percent recovery of total solids (1.51% increase). While the recovery of curd as kg 20% solids curd per kg milk showed higher values for the 0.05% SHMP than its control (0.16 increase), the difference was not great enough to be significant ($P>.05$). Therefore the addition of 0.05% SHMP to milk subsequently manufactured into cottage cheese increased the amount of curd that could be made from a given amount of milk and the recovery of milk solids. The amount of curd produced per unit of milk solids also increased, but the increase was not enough to be significant. The addition of 0.2% SHMP to milk

TABLE 11. Cottage cheese yields.[a]

Yield method	Control	0.05% SHMP	Control	0.2% SHMP
kg 20% curd per 100 kg milk	21.71	22.48*	21.82	23.07*
kg 20% curd per kg milk solids	2.02	2.18	2.13	2.25*
Percent recovery of milk solids	42.12	43.63*	42.60	45.05*

[a]Means of 8 replications.

*Significant ($P<.05$).

TABLE 12. Mean squares determining statistical significance between SHMP treated cottage cheese and their controls for yield.

		Mean Squares					
		0.05% SHMP and Control			0.2% SHMP and Control		
Source of variation	Degree of freedom	kg curd/ 100 kg milk[a]	kg curd/ kg milk solids[a]	% recovery	kg curd/ 100 kg milk[a]	kg curd/ kg milk solids	% recovery
Treatment	1	0.0324	2.3793	0.1073	0.0072	6.2375	0.0588
Replication	7	0.4743	5.2386	0.1243	0.2041	2.2219	0.0407
Treatment x Replication	7	0.0264	0.2160	0.0051	0.0872	1.0770	0.0102

subsequently manufactured into cottage cheese increased the cottage cheese yields ($P<.05$) when measured by all three methods: 1.25 kg 20% curd per 100 kg milk, 0.12 kg 20% curd per kg milk solids, and 2.45% recovery of milk solids. Due to the high fat content of the curd, these yields are higher than normally encountered. However, if the fat content of the curd, expressed as 20% solids, were subtracted from the kg 20% solids per 100 kg milk yield expression, then the values obtained should reflect regular cottage cheese. The new values for the 0.05% SHMP and control curds are respectively 17.33 and 16.91%, and the 0.2% SHMP and control respective yields as 18.74 and 16.55%. These yields are greater than the expected range of 14 to 16% (57) and still show that SHMP increased the yield of cottage cheese.

The observed effects of adding SHMP to the cottage cheese manufacturing procedure is to produce increased yields of curd containing less fat and casein, but more ash, phosphorus, calcium, and possible lactose. The fat missing in the curd appeared in the whey and is assumed to have been lost to the curd. However, the casein missing in the curd did not appear in the whey; the SHMP whey casein was 0.01 to 0.2% lower than the control whey. Because the curd yield of SHMP-treated milk increased, while increased casein was not found in the whey, the casein may have been diluted in forming more curd. Also, factors in the yield increase caused by the addition of SHMP were lactose, ash, phosphorus, and calcium. An interesting point for skimmilk cheeses such as cottage cheese is that although the addition of 0.20% SHMP decreased the fat the SHMP still increased the yield.

The whey proteins may have been a small part of the yield increase; the level of whey proteins dropped in the whey (0.01 and 0.03%) and increased in the curd (0.02 and 0.05%). Hence a small recovery of the whey proteins as curd was realized, but was not enough to be significantly different ($P<.05$) in either the curd or whey. The inability to reduce the pH of the milk to the low levels used in some of the procedures for recovering the whey proteins from whey with polyelectrolytes, pH 3.0 (34) and 3.2 (35, 75), may explain the lack of significant whey protein recovery. The desired effect was that the pH produced during the manufacture of cottage cheese (4.7) would be low enough with the quiesent coagulation of the milk to allow significant whey proteins recovery. However, the use of a pH of 3.0 to 3.2 would be undesirable to the cheese, because casein becomes increasingly soluble as the pH goes below 4.6 (66). Further studies may be needed to evaluate different properties of polyelectrolytes and cottage cheese in hopes of recovering the whey proteins. Perhaps changes in procedure such as adding the polyelectrolyte after the pH of the milk has gone down or during fortification could produce the desired changes. The possible use of polyelectrolytes in conjunction with heat treatments to the milk may be worthy of study, hoping to precipitate the whey proteins without the undesired effects of weak body and shattered curd. Finally the uses of polyelectrolytes with the direct acidification method of cottage cheese manufacture with its somewhat different environment may produce the desired effect of increased yields.

SUMMARY

The objectives of this research were to study the possibility of increasing cottage cheese yields by using the polyelectrolyte sodium hexametaphosphate to coagulate the whey proteins in the starting milk and add them to the curd. Various polyelectrolytes and levels were screened in 400 ml beakers and 3 liter laboratory vats, eventually leading to the selection of sodium hexametaphosphate at 0.05 and 0.2% to be tested against controls in 208 liter (55 gal) pilot plant vats. Fresh skimmilk, fortified with low heat nonfat dry milk was converted to cottage cheese by the short set culture method. The milk, curd, and whey were analyzed to determine total solids, fat total protein, casein whey protein, ash, phosphorus, and calcium; solids-not-fat and lactose being determined by difference. The whey and wash waters were analyzed to determine the amount of yield lost as curd fines. Finally, the cottage cheese yield was determined as kg 20% solids curd per 100 kg milk, kg 20% solids curd per kg milk solids, and as percent recovery of milk solids.

Testing the data by the least squares method of analysis of variance, the addition of 0.05% SHMP to milk manufactured into cottage cheese significantly (P<.05) increased the yields of cottage cheese when measured as kg 20% solids curd per 100 kg milk and as percent recovery of milk solids.

The addition of 0.2% SHMP to milk made into cottage cheese significantly (P<.05) increased the yields when measured by all three

methods. However, the levels of whey protein in both the curd and the whey were not significantly changed by either level of SHMP.

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APPENDIX

TABLE A-1. Composition of milk used to manufacture cottage cheese with and without 0.05% sodium hexametaphosphate.

Replication	Total solids[a]	Fat	Solids not-fat	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
	%								mg/100ml	
1	10.12	0.90	9.22	2.93	2.35	0.58	5.54	0.75	96.94	114.17
2	11.26	1.77	9.49	3.01	2.49	0.52	5.72	0.76	80.08	98.56
3	10.49	1.12	9.37	2.82	2.29	0.53	5.82	0.73	102.49	135.61
4	9.96	1.26	8.70	2.45	1.91	0.54	5.53	0.72	71.57	89.46
5	10.38	1.04	9.34	2.84	2.36	0.48	5.77	0.73	89.50	103.12
6	10.01	0.85	9.16	2.71	2.21	0.50	5.75	0.70	94.22	118.21
7	10.86	1.14	9.72	3.05	2.45	0.60	5.92	0.75	69.46	74.97
8	9.54	1.28	8.26	2.69	2.15	0.54	4.87	0.70	107.58	117.61
Average	10.33	1.17	9.16	2.81	2.28	0.54	5.62	0.73	88.98	106.46

[a]Averages of duplicate analysis.

TABLE A-2. Composition of milk used to manufacture cottage cheese with and without 0.2% sodium hexametaphosphate.

Replication	Total solids[a] (%)	Fat (%)	Solids not-fat (%)	Total protein (%)	Casein protein (%)	Whey protein (%)	Lactose (%)	Ash (%)	Phosphorus (mg/100ml)	Calcium (mg/100ml)
1	10.38	1.23	9.15	3.01	2.45	0.56	5.39	0.75	89.53	111.40
2	10.86	1.56	9.30	2.77	2.20	0.57	5.80	0.73	93.68	116.29
3	10.24	0.94	9.30	2.84	2.31	0.53	5.72	0.74	94.41	122.85
4	9.96	1.89	8.70	3.03	2.51	0.52	4.34	0.70	101.30	133.57
5	10.01	0.95	9.06	2.82	2.25	0.57	5.49	0.72	91.35	109.54
6	9.98	1.15	8.83	2.89	2.40	0.49	5.22	0.72	98.35	124.21
7	10.06	0.98	9.08	3.00	2.47	0.53	5.36	0.72	90.62	115.22
8	10.56	1.40	9.16	2.88	2.31	0.57	5.55	0.73	77.42	82.88
Average	10.26	1.26	8.99	2.91	2.36	0.54	5.36	0.73	92.08	114.50

[a]Averages of duplicate analysis.

TABLE A-3. Composition of curd resulting from the manufacture of cottage cheese without 0.05% sodium hexametaphosphate (control).

Replication	Total solids[a]	Fat	Solids not-fat	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
	%								mg/100g	
1	21.85	4.05	15.95	13.09	12.80	0.29	2.35	0.51	117.22	55.74
2	26.68	5.05	14.95	11.28	11.06	0.22	3.23	0.44	160.91	73.96
3	22.40	4.73	15.27	12.32	12.03	0.29	2.41	0.54	130.80	50.75
4	27.80	5.57	14.43	10.27	9.92	0.35	3.71	0.45	129.54	54.61
5	27.42	5.09	14.91	12.20	11.82	0.38	2.27	0.44	158.42	57.39
6	26.68	4.20	15.80	13.32	12.98	0.34	2.03	0.45	169.27	63.89
7	27.64	5.30	14.70	11.62	11.47	0.15	2.54	0.54	263.54	135.70
8	28.58	4.41	15.59	11.84	11.64	0.20	3.27	0.48	181.79	69.26
Average	26.14	4.80	15.20	11.99	11.72	0.28	2.73	0.48	163.94	70.16

[a]Averages of duplicate analysis.

TABLE A-4. Composition of curd resulting from the manufacture of cottage cheese with 0.05% sodium hexametaphosphate.

Replication	Total solids[a]	Fat	Solids not-fat	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
	%								mg/100g	
1	22.00	3.79	16.21	12.40	12.02	0.38	2.92	0.89	212.46	129.80
2	23.63	6.33	13.67	9.82	9.44	0.38	2.93	0.92	212.39	141.34
3	22.80	5.24	14.76	11.67	11.23	0.44	2.28	0.81	210.32	119.87
4	26.77	5.59	14.41	11.32	10.95	0.37	2.42	0.67	240.44	139.52
5	27.02	5.33	14.67	9.89	9.57	0.32	4.01	0.77	227.44	132.24
6	27.69	4.46	15.54	10.36	10.03	0.33	4.51	0.67	256.18	141.72
7	26.54	5.77	14.23	11.42	11.28	0.14	2.02	0.79	264.23	153.04
8	26.45	4.70	15.30	11.30	11.00	0.30	3.23	0.77	256.95	136.13
Average	25.36	5.15	14.85	11.02	10.69	0.33	3.04	0.79	235.05	136.71

[a]Averages of duplicate analysis.

TABLE A-5. Composition of curd resulting from the manufacture of cottage cheese without 0.2% sodium hexametaphosphate (control).

Replication	Total solids[a]	Fat	Solids not-fat	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
	%								mg/100g	
1	24.14	5.07	14.93	13.10	12.80	0.30	1.27	0.56	124.89	60.93
2	21.31	5.54	14.46	13.79	13.50	0.29	0.15	0.52	147.40	56.44
3	26.07	5.00	15.00	13.11	12.89	0.22	1.37	0.52	153.07	62.72
4	25.78	5.43	14.57	11.81	11.45	0.36	2.13	0.63	210.68	122.05
5	26.50	5.90	14.10	13.20	12.88	0.32	0.36	0.54	144.52	59.18
6	24.54	4.89	15.11	12.49	12.12	0.37	2.19	0.43	142.48	54.70
7	25.31	4.76	15.24	13.18	12.82	0.36	1.56	0.50	155.04	60.39
8	23.10	5.60	14.40	11.91	11.39	0.52	2.05	0.44	128.80	58.09
Average	24.59	5.27	14.73	12.82	12.48	0.34	1.39	0.52	150.86	66.81

[a] Averages of duplicate analysis.

TABLE A-6. Composition of curd resulting from the manufacture of cottage cheese with 0.2% sodium hexametaphosphate.

Replication	Total solids[a]	Fat	Solids not-fat	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
	%								mg/100g	
1	21.60	5.32	14.68	10.10	9.71	0.39	3.08	1.50	419.50	291.08
2	22.05	5.19	14.81	10.62	10.24	0.38	3.14	1.05	273.19	163.70
3	23.82	3.42	16.58	11.99	11.60	0.39	3.20	1.39	340.21	231.13
4	23.02	4.26	15.74	9.59	9.08	0.51	4.93	1.22	320.61	216.76
5	28.54	3.78	16.22	11.35	11.25	0.10	3.65	1.22	455.10	280.02
6	26.12	4.24	15.76	11.12	10.80	0.32	3.55	1.09	408.11	248.04
7	28.88	3.89	16.11	11.47	11.10	0.37	3.32	1.32	478.00	293.40
8	25.01	4.51	15.49	9.82	9.36	0.46	4.58	1.09	353.34	203.18
Average	24.88	4.33	15.67	10.76	10.39	0.36	3.68	1.24	381.01	240.91

[a]Averages of duplicate analysis.

TABLE A-7. Composition of whey resulting from the manufacture of cottage cheese without 0.05% sodium hexametaphosphate.

Replication	Total solids[a]	Fat	Solids not-fat	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
	%								mg/100ml	
1	7.04	0.19	6.85	0.53	0.14	0.39	5.58	0.74	75.21	116.00
2	7.75	0.41	7.34	0.64	0.17	0.47	6.02	0.68	75.37	111.57
3	7.37	0.27	7.10	0.54	0.02	0.52	5.79	0.77	77.74	114.71
4	4.84	0.39	4.45	0.62	0.16	0.46	3.36	0.47	64.59	96.42
5	6.96	0.11	6.85	0.49	0.02	0.47	5.68	0.68	77.11	112.80
6	6.89	0.16	6.73	0.57	0.07	0.50	5.49	0.67	66.98	106.09
7	7.07	0.19	6.88	0.51	0.03	0.48	5.74	0.63	75.48	105.12
8	6.35	0.20	6.15	0.47	0.04	0.43	5.03	0.65	78.98	112.27
Average	6.78	0.24	6.54	0.55	0.08	0.46	5.34	0.66	73.93	109.37

[a] Average of duplicate analysis.

TABLE A-8. Composition of whey resulting from the manufacture of cottage cheese with 0.05% sodium hexametaphosphate.

Replication	Total solids[a]	Fat	Solids not-fat	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
	%								mg/100ml	
1	7.00	0.25	6.75	0.53	0.04	0.49	5.52	0.70	78.74	101.44
2	7.36	0.28	7.08	0.54	0.10	0.44	5.83	0.71	81.53	95.74
3	7.39	0.33	7.06	0.57	0.03	0.54	5.67	0.82	77.40	106.85
4	6.85	0.22	6.63	0.51	0.03	0.48	5.39	0.73	81.27	99.82
5	6.43	0.08	6.35	0.47	0.06	0.41	5.22	0.66	74.89	104.30
6	5.82	0.21	5.61	0.40	0.04	0.36	4.57	0.64	74.67	101.27
7	6.92	0.17	6.75	0.59	0.14	0.45	5.47	0.69	75.23	112.18
8	5.96	0.23	5.73	0.45	0.01	0.44	4.73	0.55	64.22	81.66
Average	6.72	0.22	6.50	0.51	0.06	0.45	5.30	0.69	75.99	100.41

[a]Averages of duplicate analysis.

TABLE A-9. Composition of whey resulting from the manufacture of cottage cheese without 0.2% sodium hexametaphosphate.

Replication	Total solids[a]	Fat	Solids not-fat	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
	%								mg/100ml	
1	7.17	0.24	6.93	0.58	0.13	0.45	5.57	0.78	96.41	82.02
2	7.28	0.36	6.92	0.57	0.08	0.49	5.63	0.72	73.19	111.61
3	6.97	0.21	6.76	0.53	0.09	0.44	5.47	0.76	61.75	90.81
4	6.32	0.28	6.04	0.49	0.04	0.45	4.87	0.68	63.70	105.46
5	6.04	0.20	5.84	0.47	0.09	0.38	4.80	0.57	72.26	110.47
6	6.66	0.23	6.43	0.49	0.07	0.42	5.22	0.72	74.86	107.27
7	6.55	0.17	6.38	0.46	0.05	0.41	5.20	0.72	69.85	114.96
8	6.42	0.18	6.24	0.49	0.12	0.37	5.13	0.62	76.23	110.98
Average	6.68	0.23	6.44	0.51	0.08	0.43	5.24	0.70	73.53	104.20

[a]Average of duplicate analysis.

TABLE A-10. Composition of whey resulting from the manufacture of cottage cheese with 0.2% sodium hexametaphosphate.

Replication	Total solids[a]	Fat	Solids not-fat	Total protein	Casein protein	Whey protein	Lactose	Ash	Phosphorus	Calcium
	%								mg/100ml	
1	7.47	0.22	7.25	0.58	0.10	0.57	5.92	0.75	86.54	74.19
2	7.52	0.51	7.01	0.46	0.04	0.42	5.75	0.80	100.07	73.40
3	7.26	0.38	6.88	0.53	0.17	0.36	5.56	0.79	85.56	101.77
4	6.51	0.51	6.00	0.46	0.07	0.39	4.83	0.71	63.62	96.74
5	6.15	0.33	5.82	0.40	0.06	0.34	4.87	0.55	99.92	85.75
6	7.22	0.30	6.92	0.47	0.11	0.36	5.72	0.73	98.02	78.18
7	6.50	0.43	6.07	0.50	0.05	0.45	4.85	0.72	68.40	57.77
8	7.22	0.24	6.98	0.48	0.13	0.35	5.74	0.76	95.80	78.20
Average	6.98	0.36	6.62	0.48	0.09	0.40	5.41	0.73	87.24	80.75

[a]Average of duplicate analysis.

TABLE A-11. Total yield lost as curd fines for cottage cheese made with and without 0.05% sodium hexametaphosphate (SHMP).[a]

Replication	Control			0.05% SHMP		
	Whey	1st Wash	2nd Wash	Whey	1st Wash	2nd Wash
1	0.65	0.39	0.08	1.14	0.11	0.20
2	0.81	0.06	0.09	0.51	0.70	0.13
3	0.45	0.17	0.13	0.44	0.13	0.13
4	0.44	0.30	0.16	0.55	0.42	0.29
5	1.38	0.56	0.42	1.76	0.24	0.16
6	0.55	0.13	0.24	0.41	0.18	0.28
7	0.49	0.24	0.18	0.32	0.04	0.40
8	0.57	0.14	0.13	0.68	0.14	0.22
Average	0.67	0.25	0.18	0.73	0.24	0.23

[a]Calculated as kg 20% solids curd per 100 kg milk.

TABLE A-12. Total yield lost as curd fines for cottage cheese made with and without 0.2% sodium hexametaphosphate (SHMP).[a]

Replication	Control			0.2% SHMP		
	Whey	1st Wash	2nd Wash	Whey	1st Wash	2nd Wash
1	1.68	0.20	0.21	0.99	0.05	0.15
2	0.44	0.32	0.11	0.64	0.15	0.13
3	0.49	0.25	0.125	0.37	0.31	0.16
4	0.54	0.17	0.27	0.32	0.22	0.21
5	0.38	0.14	0.18	0.59	0.30	0.16
6	0.46	0.18	0.27	0.71	0.31	0.19
7	0.29	0.10	0.26	0.05	0.19	0.19
8	0.58	0.23	0.18	0.70	0.35	0.27
Average	0.61	0.20	0.20	0.55	0.24	0.18

[a]Calculated as kg 20% solids curd per 100 kg milk.

TABLE A-13. Yields of cottage cheese made with and without 0.05% sodium hexametaphosphate (SHMP).

Replication	Control: kg 20% curd/ 100 kg milk	Control: kg 20% curd/ kg solids	Control: Recovery of solids %	0.05% SHMP: kg 20% curd/ 100 kg milk	0.05% SHMP: kg 20% curd/ kg solids	0.05% SHMP: Recovery of solids %
1	20.29	2.00	40.10	21.30	2.10	42.10
2	20.78	1.84	36.89	21.67	1.92	38.51
3	20.62	1.97	39.34	21.17	2.02	40.35
4	23.39	2.35	46.95	23.80	2.39	47.80
5	24.37	2.35	46.97	24.84	2.39	47.86
6	19.12	1.19	38.19	21.38	2.14	42.70
7	23.47	2.16	43.18	23.80	2.19	43.83
8	21.62	2.27	45.34	21.87	2.29	45.86
Average	21.71	2.02	42.12	22.48	2.18	43.63

TABLE A-14. Yields of cottage cheese made with and without 0.2% sodium hexametaphosphate (SHMP).

Replication	Control			0.2% SHMP		
	kg 20% curd/ 100 kg milk	kg 20% curd/ kg solids	Recovery of solids %	kg 20% curd/ 100 kg milk	kg 20% curd/ kg solids	Recovery of solids %
1	22.88	2.20	44.08	23.48	2.26	45.24
2	22.05	2.03	40.59	22.94	2.11	42.24
3	21.38	2.09	41.76	21.77	2.13	42.51
4	24.55	2.46	49.29	23.20	2.33	46.60
5	21.73	2.17	43.40	23.86	2.38	47.68
6	20.99	2.10	42.04	22.80	2.28	45.70
7	21.39	2.13	42.50	24.98	2.48	49.65
8	19.62	1.86	37.14	21.55	2.04	40.81
Average	21.82	2.13	42.60	23.07	2.25	45.05